## Autoclave Test for Constancy of Volume of Cement.

A MEETING of United States cement manufacturers, held at Chicago on February 18 on the invitation of the American Portland Cement Association, decided to adopt the autoclave test as a criterion of volume constancy throughout the industry. As soon as the necessary testing equipment can be installed, no cement is to be supplied that shows an expansion greater than 1 per cent. in an autoclave test of a 1 in. by 1 in. bar either 5 in. or 10 in. long.

Studies of a modified autoclave test procedure have been under way for some years past, and it is felt that sufficient test results are available to indicate that the test has merit although it has not yet been fully correlated with experience in construction. By adopting the autoclave test, cement manufacturers hope to guard against any possibility of unsoundness in cement not revealed by the present standard tests.

### Method of Testing.

The test procedure is described as follows :

Mix a neat cement paste of normal consistency in accordance with the methods described in Sections 19 to 22 of " Standard Methods of Sampling and Testing Portland Cement " (A.S.T.M. designation C77-32). Immediately after mixing, fill the mould in three layers, compacting each layer by hand with the rubber-glove-protected forefinger. Starting at one end of the mould, work along the bar, reaching the opposite end in 25 strokes. Work along the bar and back twice, or a total of four times for each layer. After the top layer has been compacted the specimen should be smoothed off with a few strokes of the trowel, leaving the paste slightly above the sides of the mould.

Immediately after the mould has been filled, cover it with damp hessian, taking care that the hessian does not come in direct contact with the specimen. Approximately 2 hours after moulding, the specimen should be given the final trowelled finish and the identifying reference numbers inscribed on the surface by

means of steel dies. The specimens in the moulds should then be placed in a moist closet.

Twenty-two hours after moulding, remove the specimens from the moulds and place them in water at 80 deg. F. Approximately 1 hour after removal from moulds the specimens, one at a time, should be surface dried with a cloth and immediately weighed and measured for length in a length comparator. After weighing and measuring, the specimens should be kept in water until placed in the autoclave at the age of 24 hours.

Place the bars in the autoclave which has been provided with the proper amount of water ; raise the temperature from 80 deg. F. to 420 deg. F. in one hour. Maintain the 420 deg. F. temperature for a period of three hours, then allow the steam pressure to drop to 0 to 5 lb. gauge pressure in one hour.

Remove the cover from the autoclave and allow the bars to cool in the autoclave for 15 minutes. Then remove the bars and allow them to cool in the air of the laboratory for another 15 minutes until they reach a temperature of about 150 to 180 deg. F. during a half-hour period. Surface dry the bars and measure for length and weight.

Examination of many types and makes of cement for volume change has revealed large differences in expansion under continued exposure to water. When the rate of expansion is large it is usually progressive and the cement proves unsound. The factors responsible for this condition are not yet fully understood. The regular use of the autoclave expansion test, however, is claimed to eliminate cases of excessive expansion and will probably lead also to progressive reduction in variation of expansion in commercial cement practice.

# Resistance of Portland Cement to Sulphate.

A NUMBER of tests made in connection with a hydro-electric scheme in Maine, U.S.A., showed that Portland cements of medium high fineness and low calcium aluminate content gave excellent strengths in reasonably short periods, were resistant to magnesium sulphate attack, and had low volume change under both alternate wetting and drying and freezing and thawing. Portland cements with high calcium aluminate content, on the other hand, did not withstand sulphate attack and showed large volume change. The high-early-strength cements were satisfactory. An alumina cement gave excellent performance throughout. A Portland-pozzolana cement showed reasonable strength and gave high resistance to sulphate, but performed poorly under alternate freezing and thawing.

Studies made with respect to the use of salt water both in mixing and curing gave some interesting results. Sea water accelerated setting as compared with fresh water, but this action was attained at the expense of ultimate strength and durability. Such concrete was less resistant to freezing and thawing. However, it was indicated that no damaging effects would result from the use of salt water for curing, provided that the film of salt deposited on horizontal construction joints was thoroughly cleaned off prior to concreting the next lift.

# Direct Firing of Rotary Kilns.

Some results of experience in direct firing of rotary kilns in United States cement plants are given by Mr. R. M. Hardgrove, of the Babcock & Wilcox Co., of New York, in a recent number of *Rock Products*. During the years 1927 to 1930, eight direct-fired kiln installations using Fuller Bonnot pulverisers were put into operation and have given satisfactory results. The following is an abstract of Mr. Hardgrove's article.

## Economies in Labour, Power and Fuel.

With direct firing the kiln operator also operates the pulverisers, thus saving the labour required in the coal house. An average cost of labour for a separate coal house, plus maintenance of dryers and other equipment (except pulverisers), is about 1.2 cents per barrel. Elimination of the power required for dryers, dryer fans, transport systems, and feeders saves 4 kW-hours per ton of coal.

There is a saving of from $\frac{1}{2}$ to 1 per cent. of the coal used for firing the dryers, to which vent losses must be added. Modern direct-fired installations show a saving of 10 to 15 lb. per barrel in coal consumption compared with storage-system operation of the same kilns.

## Cleanliness and Safety.

With direct firing there are no vents emitting coal dust, and the dirt and nuisance of emptying the bins are avoided. Explosions and overflowing of bins resulting in fires are almost entirely eliminated, as the pulverised coal is used as soon as it is produced and the air in a pulveriser is too rich in coal to support combustion. The pulveriser and piping are all of welded steel construction of ample strength to withstand any pressure that may result from an explosion.

## Operation.

In a direct-firing system the coal is uniformly dispersed in the primary air, and each particle is surrounded by air ready to be ignited and to burn with a large amount of surface exposed. A fineness of 80 to 85 per cent. through a 200-mesh sieve—with 99.5 per cent. through a 50-mesh sieve—is desirable for the best results, and direct-firing pulverisers will produce that fineness throughout the life of the grinding elements. The heat in the clinkering zone is transmitted to the clinker largely by the radiation from the carbon particles, and is directly proportional to the surface of the particles. Thus, fine pulverisation is desirable because it results in early stable ignition and complete combustion, and also because it increases the transfer of heat to the clinker.

Ignition is earlier with direct firing than with storage firing, even though the fineness and air velocities are approximately the same. This is due to the better dispersion of the coal in the air. The addition of moisture to gaseous fuels has a decided tendency to speed up the ignition, and it seems reasonable that it has a similar effect on the gases distilled from pulverised coal. The factors controlling ignition are the temperature of the air and coal, the velocity of the coal and

air at the burner tip, and the amount of air per pound of coal. The maximum speed of ignition is reached at from 3 to 5 lb. of air per pound of coal, which is the amount used by direct-firing pulverisers. This larger amount of primary air is also necessary properly to dry very wet coal. For 3 lb. of primary air per pound of coal the temperature of the air at the burner should not exceed 180 deg. F. and the velocity should not be less than 7,500 ft. per minute. The limits given are those prevailing with a kiln having a Unax cooler and giving ignition close to the burner tip. The ignition can be allowed to draw away from the tip somewhat without becoming unstable ; that is, velocities higher than 7,500 ft. per minute and temperatures lower than 180 deg. F. can be used. Other types of kilns having shorter burners permit lower velocities and higher air temperatures.

TABLE I.—HEAT BALANCE TESTS.

|  | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 |
|---|---|---|---|---|---|
| Duration .. .. .. | 49.6 hours | 24 hours | 24 hours | 30 days | 12 hours |
| Kiln size (ft.) .. .. .. | 10 × 100 | 10 × 100 | 10 × 100 | 10 × 280 | 10 × 150 |
| Barrels per hour .. .. | 47.9 | 51.29 | 51.0 | 72.9 | 8.54 T |
| Coal, lb. per hour . .. | 5,772 | 5,346 | 5,260 | 6,656 | 6,142 |
| Coal, lb. per barrel .. .. | 120.3 | 104.21 | 103.34 | 91.3 | 53.94/100 |
| Fineness of coal, % on 200-mesh sieve .. .. .. | — | 79.2 | 78.3 | 85.2 | 83.0 |
| Million B.T.U. per barrel .. | 1.17 | 1.04 | 1.025 | 1.19 | — |
| Primary air, per cent. .. .. | 25.5 | 36.4 | 38.3 | — | — |
| Waste-heat steam, lb. per barrel | 433.2 | 278.6 | 265.7 | — | — |
| | | | | | |
| Temperature of primary air .. | 146 | 137 | 140 | 173 | 166 |
| ,, of secondary air .. | 1,023 | 1,100 | 1,160 | 1,210 | 1,375 |
| ,, of kiln exit .. | 1,860 | 1,768 | 1,763 | 646 | 1,500 |
| ,, of stack .. .. | 366 | 361 | 358 | — | — |
| ,, of air to pulveriser | 450 | 400 | 400 | — | 273 |
| ,, of kiln front .. | 2,660 | 2,815 | 2,834 | — | — |
| | | | | | |
| Coal analysis : | | | | | |
| Moisture .. .. .. | 16.7 | 11.3 | 13.1 | 4.86 | 4.4 |
| Ash .. .. .. .. | 8.39 | 18.18 | 19.52 | 12.9 | 7.5 |
| Sulphur .. .. .. | 1.67 | 4.36 | | 0.9 | 0.9 |
| Volatile .. .. .. | 34.23 | 37.33 | | 29.1 | 35.9 |
| B.T.U. as fired .. .. | 9,705 | 9,974 | | 13,033 | 13,317 |
| | | | | | |
| Heat Input, per cent. : | | | | | |
| Fuel .. .. .. .. | 81.14 | 82.69 | 82.21 | 83.68 | 84.78 |
| Air .. .. .. .. | 12.87 | 10.54 | 10.74 | 11.35 | 14.50 |
| Exothermic .. .. .. | 4.55 | 5.15 | 5.36 | 4.59 | 0.72 |
| Raw feed .. .. .. | 1.44 | 1.62 | 1.69 | 0.38 | — |
| | | | | | |
| Heat output, per cent. : | | | | | |
| Calcination and dehydration | 26.44 | 29.74 | 30.93 | 26.94 | 27.39 |
| Dry waste gases .. .. | 40.95 | 36.35 | 36.53 | 9.94 | 30.45 |
| $H_2O$, Sensible, latent, and superheat .. .. .. | 9.04 | 8.33 | 8.77 | 31.59 | 11.62 |
| CO .. .. .. .. | 0.36 | 1.69 | 0.04 | 0 | 0.22 |
| Dust .. .. .. .. | 2.01 | 1.49 | 1.55 | 0.15 | 0.42 |
| Clinker .. .. .. | 15.32 | 17.36 | 18.06 | 14.68 | 10.91 |
| Radiation and unaccounted for .. . .. .. | 5.88 | 5.04 | 4.07 | 16.70 | 16.17 |
| | | | | Air leakage at hood | 2.82 |

The fineness and quantity of coal withdrawn from a direct-firing pulveriser are controlled by the quantity of air used. As this may not give the desired velocity at the burner tip, a by-pass is provided around the pulveriser so that additional air can be introduced into the burner line as desired. The earliest possible ignition that will not burn up the tip or result in undue damage to the kiln lining will give the most efficient operation, as it results in increasing the effective length of the kiln. Illinois coal having 19.8 per cent. moisture has been successfully fired, and the output and coal rate are better than were obtained with the storage system.

## Heat Balances.

Abstracts from five heat balances on direct-fired kilns are given in Table 1. In test No. 1 an attempt was made to generate more steam, with the result that the amount of coal and B.T.U. per barrel are higher than usual. The B.T.U. per barrel rates for tests Nos. 2 and 3 using high-moisture Illinois coal are creditable. A good indication of the accuracy of the tests and the uniformity of feed is given in the consistency of the radiation and unaccounted-for losses for the first three tests. The kiln used in tests Nos. 1, 2, and 3 is a dry-process kiln equipped with a Lee cooler. The kiln used in test No. 4 is a wet-process kiln,

TABLE 2.—COAL CONSUMPTION.

|  | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 | No. 6 |
|---|---|---|---|---|---|---|
| Lb. coal per barrel, storage system .. .. .. | 121 | 134 | 105 | 130 | — | — |
| Lb. coal per barrel, direct fired .. .. .. | 111 | 115 | 91 | 125 | — | — |
| Lb. coal per 100 lb. material, storage .. .. .. | — | — | — | — | 63 | 56 |
| Lb. coal per 100 lb. material, direct .. .. .. | — | — | — | — | 48 | 38 |
| Kiln output, barrels per hour, storage .. .. | 40 | — | 68 | — | 60 T/day | 170 T/day |
| Kiln output, barrels per hour, direct .. .. | 40 | 51 | 72 | 54 | 80 T/day | 205 |
| Size of kiln (ft.) .. .. | 10 × 175 | 10 × 100 | 10 × 280 | 9 × 130 | 8 × 150 | 10 × 150 |
| Process .. .. .. | Wet | Dry | Wet | Dry | Dry | Semi-wet |
| Coolers .. .. .. | Unax | Lee | Rot | Lee | Rot | Vanderwerp |

equipped with a rotary cooler. These differences should be kept in mind in comparing the B.T.U. rates and the radiation losses. The radiation losses would be expected to be higher with the longer kilns.

Table 2 gives the coal saving made after the installation of direct firing in six plants. The savings for the two Dolomite installations (Nos. 5 and 6) are expressed as pounds per 100 lb. of product and are on a different basis from those for the cement kilns. The relative coal rates are, however, comparative.

## Type of Coal.

In general, the quality of coal required for direct firing a kiln is the same as that needed for storage systems. High-moisture coals of fine size are difficult

to handle in a rotary dryer but can be used successfully in a direct-firing system. In No. 4 (Table 2), a very fine coal, practically all passing a 50-mesh sieve, is available at an appreciably lower cost and is used successfully. The only trouble encountered was in maintaining the flow from the bin when the coal was wet; this difficulty was overcome by constructing a jacket around the bin through which hot air from the Lee cooler is circulated.

### Maintenance.

Coals high in ash offer no special difficulty and, as shown in Table 1, coals having 18 to 19 per cent. ash are used. At one time during the tests the ash content was as high as 24.4 per cent., but caused no difficulty. The sulphur content of the coal used in the tests was 4.3 per cent. Where it is economical
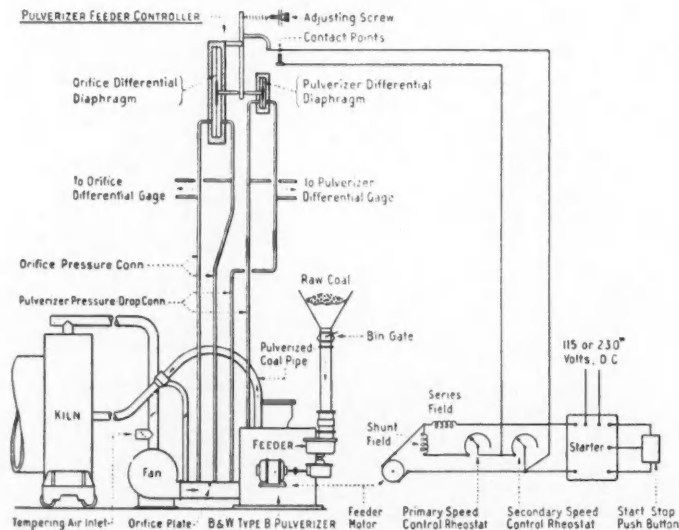


**Fig. 1.—Diagrammatic Arrangement of Automatic Control System.**

to do so coals of this quality can be used, but it cannot be expected that maintenance on the pulveriser will be as low as is obtained with better-grade coals. The fact that some coals cause fifteen times as much wear as others proves that it is the coal and its impurities which wear out the grinding elements.

With grinding elements lasting from 4,000 to 40,000 hours or more, depending on the coal, the cost per ton of output for these parts varies from 3 cents to 0.3 cent per barrel. Also, there is less trouble from rings in kilns, as the very close control of coal feed permits the operator to run slightly reducing or slightly oxidising at will.

## Pulveriser Feeder Control.

Raw coal is much easier to feed evenly than pulverised coal, but combustion conditions in a kiln can and should be adjusted so that feeding a constant volume of raw coal is not sufficient, as variation in moisture and size affect the heating value of a given volume of coal. *Fig.* 1 shows a pulveriser feeder controller that has proved successful in delivering a uniform flow of coal to the kiln. During two tests of twelve hours' duration the largest deviation in hourly weights was 8 lb., or 0.13 per cent. The controller maintains a definite ratio between the air flow, which is measured by an orifice in the clean air line, and the pressure drop through the pulveriser ; thus a definite amount of coal is maintained in the pulveriser for a given air flow. If too much coal accumulates in the pulveriser,
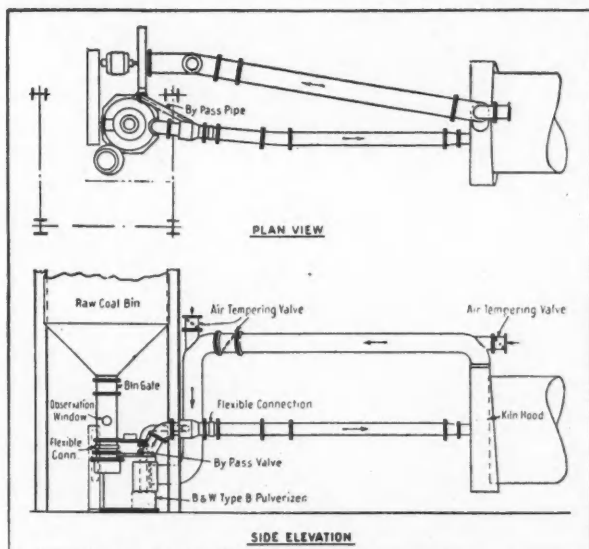


Fig. 2.—Example of Direct Firing as Installed at a Cement Works.

the pressure drop through the pulveriser increases. This unbalances the opposed diaphragms and closes an electrical contact that shunts out the secondary rheostat, thus reducing the speed of the direct-current motor driving the feeder. When the coal level drops and the diaphragms become balanced the contact opens. The feeder speed is thus varied between two points to maintain the desired coal levels in the pulveriser. Increases in the amount of coal delivered are obtained by increasing the air flow by means of a damper in the primary air line. This is the only adjustment necessary to vary the coal rate. The primary and secondary rheostats are adjusted to give feeder speeds well above and well below the operating range. Variations in voltage or motor temperature do not affect the accuracy of the control so long as the range is wide enough. Signal lights on the front of
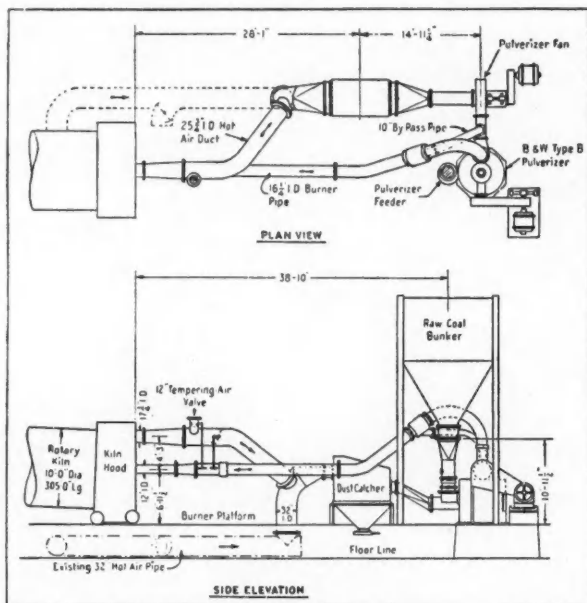
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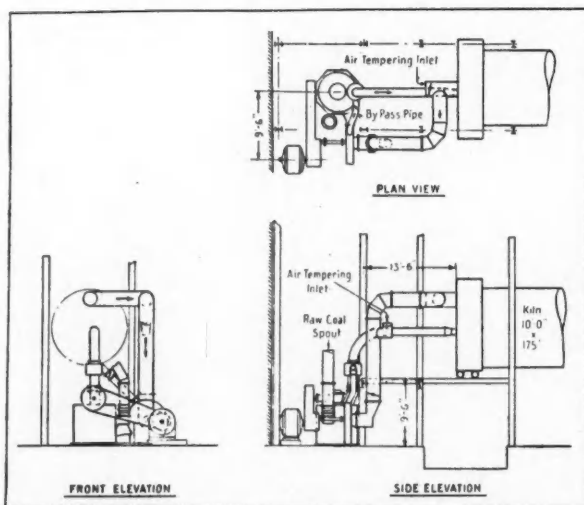Fig. 3.—Example of Direct Firing as Installed at a Cement Works.

Fig. 4.—Installation on Two Kilns at a Cement Works.

the controller indicate high and low speed operation, enabling the operator to tell by the frequency of the change in lights if the speed range is ample. The small diaphragm can be adjusted vertically to obtain the desired ratio for each installation, and the small spring can be varied to give the proper relation between air and coal at various outputs. When once adjusted the ratio of coal to air will always be the same for a given rate of air flow, making it impossible to overload or choke the pulveriser. As increased coal output is obtained by increasing the air flow the response to changing load is very rapid, a characteristic that is very desirable with fluctuating boiler loads but is not so necessary with kiln firing.
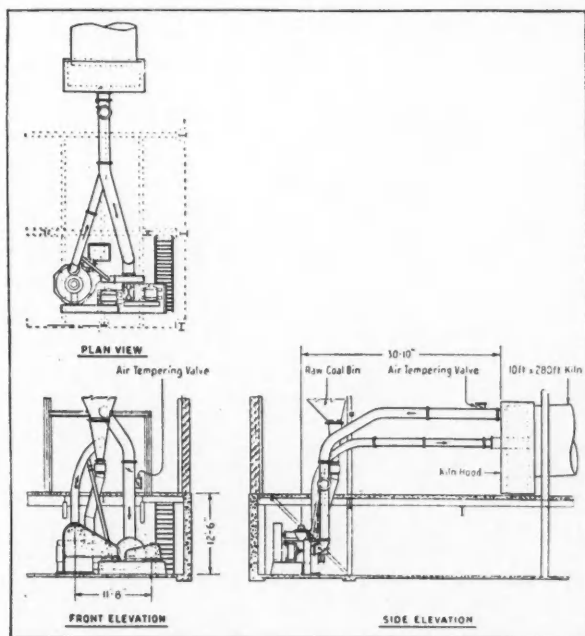


**Fig. 5.—Arrangement at Works No. 4 in Table 1 and No. 3 in Table 2.**

For firing steam boilers the control is used with a squirrel-cage constant-speed feeder-motor that is stopped and started as required. This arrangement gives even quicker response to fluctuations in load than the direct-current motor, but the latter varying through a much smaller speed range has seemed preferable for kiln firing where direct current is available.

## Source of Hot Air.

The primary air must be heated sufficiently to evaporate the surface moisture of the coal and still be safely above the dew-point. Usually the dew-point of the

air leaving the pulveriser is reached at about 110 to 120 deg. F. and enough additional heat is supplied to maintain a temperature of 140 to 160 deg., which is still well below the ignition limit mentioned. With the air in sufficient quantity and at the proper temperature to dry the coal, the capacity of the pulveriser and the fineness of its output are the same as when handling dry coal. The air quantity, which is about 3 lb. of air per pound of coal, is more than is used in some other types of direct-firing pulverisers and is one of the reasons why coal having moisture as high as 19.8 per cent. can be successfully handled. This large weight of air, even with the air cold at starting, has an appreciable drying effect and permits warming up a kiln more rapidly. Ordinarily a temperature of 400 deg. F. for the air entering the pulveriser will be ample, but for Illinois coal air at 500 deg. F. has been used to advantage. This hot air is most conveniently obtained from the kiln hood, where temperatures of about 1,200 deg. F. usually exist. Tempering air is admitted as required to maintain the air leaving the pulveriser at the desired temperature. The hot air has been taken from the top of the hood in some installations and from the front of the hood near the top on others. Probably the top position is to be preferred, as it is easier to disconnect the piping when necessary to move the hood and there may be less grit drawn into the fan with the air. Where Lee coolers are used the hot air is taken from the duct between the cooler and the burner. Dust collectors or settling chambers have been installed at some plants ; at another plant a jacket is being placed around the hot end of the rotary cooler from which the hot air is drawn.
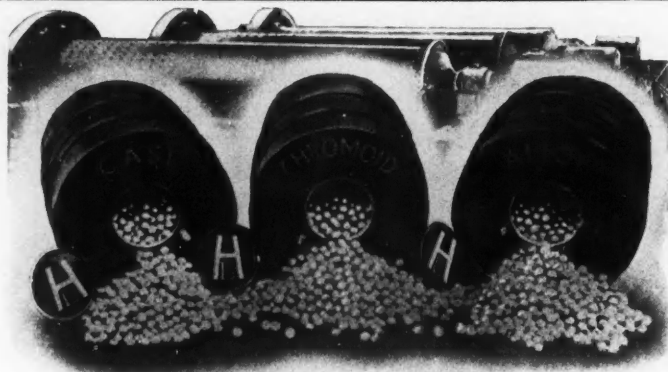
# The Design and Operation of Modern Lime Works—V.*

### By N. V. S. KNIBBS, D.Sc.

#### (*Continued.*)

HEIGHT OF KILNS.—The time of passage through a kiln depends on the total capacity and the rate of drawing and is indepenent of the length of the shaft. Thus a kiln of 2,000 cu. ft. capacity could be built 6 ft. in diameter and 71 ft. high or 12 ft. in diameter and 18 ft. high. What determines the economic height of such a kiln ?   There are twelve major factors, five of which favour a long shaft and seven a short shaft, and the optimum height is therefore a compromise between opposing claims.   In favour of a tall narrow kiln there are : (*a*) Better heat transference and therefore higher efficiency ; (*b*) Evenness of passage of stone and lime down the kiln, with which is associated simplicity of design of charging and discharging arrangements ; (*c*) Evenness of the upward passage of air and gases ; (*d*) In a gas-fired kiln, ease of even gas distribution ; and (*e*) In a mixed-feed kiln ease of fuel distribution.   In favour of a short wide kiln are : (*p*) Low power consumption ; (*q*) Less crushing of the lime ; (*r*) Lower capital and maintenance cost of refractory lining ; (*s*) Lower cost of the kiln as a whole ; (*t*) Lower heat-losses through the kiln walls ; (*u*) Lower cost of raising the stone (and fuel) for charging, and (*v*) Peripheral voids are less.

(*a*) *Heat Transference.*—The incidence of the length of the shaft on thermal efficiency requires consideration.   Closely associated with it is its influence on the combustion of the fuel in a mixed-feed kiln, but a discussion of the latter will be deferred until the theory of mixed-feed kilns is considered.   In the kiln there are two streams of material, one gas and the other solid, flowing counter-current and exchanging heat.   The time they are in contact is independent of the length of the kiln shaft—it depends only on capacity—and therefore if the rate of heat transference were the same there would be no advantage in the longer shaft.   Heat transference is due partly to radiation from the solid to the gases and *vice versa*, and partly to conduction and convection, and in the pre-heating and cooling zones the latter mode of exchange is the more important. On solid bodies there is a " skin " of stagnant gas of relatively low thermal conductivity, and this layer of gas restricts heat transference by conduction and convection.   When the gas velocity is low the layer is of maximum thickness and heat exchange is at a minimum, whilst as the velocity increases the layer diminishes and the rate of heat transference is increased.   It has been shown (*Furnas, J. Ind. Eng. Chem.*, 22, 721, 1930) that under conditions similar to those in the upper parts of a lime kiln the rate of heat transference varies approximately in proportion to the 0.7 power of the velocity.   In two kilns of the same capacity, one having double the height of the other, the gas velocity in the tall kiln will be twice that in the short one and therefore the rate of heat transference in the

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* For previous articles in this series see our issues for January, February, March and April, 1937.

preheating zone of the tall kiln will be $2^{0.7} = 1.6$ times that in the short kiln. In the burning zone conditions are different in that radiation is a more important factor in heat transference, and the higher the burning temperature the more important does it become. Moreover, the evolution of gas from the surface of the lime will slightly influence heat transference, reducing convection transference and therefore increasing the relative importance of radiation. In the burning zone, therefore, length has less influence on efficiency than in the preheating zone ; but it has some effect, and this diminishes as the temperature is raised. In the lime-cooling zone Furnas's factor would apply were it not for the fact that lime is a poor conductor of heat ; the transference of heat from inside the lumps to the surface is relatively of much more importance than in limestone, and this diminishes the influence of air velocity. In the whole kiln, therefore, the influence of velocity is important, but is much less than that of its 0.7 power, and the actual effect varies with different burning conditions. Because its greatest effect is in the preheating zone, which has least influence on the total kiln efficiency, and least in the burning zone which has the greatest influence on the efficiency, the influence of height is less than might be expected. The effect may be of the order of the 0.4 power of the velocity. Modern kilns to burn 6-in. stone have an effective shaft length of at least 40 ft. and, as already mentioned, it is to such kilns that *Fig.* 16* applies. If a kiln were required of half that height the velocity would be halved and the overall rate of heat transfer would then be of the order of $\dfrac{1}{2^{0.4}} = \dfrac{1}{1.33} = 0.75$, so that the capacity of the shaft, to maintain the same efficiency, would have to be increased by about one-third.

(*b*) and (*c*) *Passage of Material and Gases.*—The effective height of a kiln shaft is that part of it through which stone and lime descend and air and gases ascend uniformly over the whole cross-sectional area. It is obvious that the difficulties of attaining even flow are increased greatly as the ratio of diameter to height is increased, especially when mechanical charging is employed. The devices available for attaining even flow of solids and gases have already been discussed, and reference to them gives some idea of the difficulties of the design of a short wide kiln. Modern kilns, as they have become more and more mechanical, have tended to increase in height largely because of these inherent difficulties, although the difficulties are not unsurmountable.

(*d*) *Gas Distribution.*—The uniform distribution of gas over the whole area of a kiln shaft was one of the fundamental problems of gas-fired lime kilns, and here again it is obvious that the difficulty increases as the ratio of height to diameter decreases. The discussion of how gas distribution is attained will be deferred until the design of gas kilns is considered, but it may be said here that distribution over a short wide shaft is at present impracticable.

(*e*) *Fuel Distribution.*—In a mixed-feed kiln, on the other hand, even fuel distribution over a wide shaft, though undoubtedly more difficult to effect

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* *Cement and Lime Manufacture*, April, 1937, page 125.

mechanically, is by no means impracticable, and this disadvantage of the short kiln is not serious.

Of the five factors favouring a tall kiln those concerned with the even passage through the shaft are of most weight. Advantages of tall kilns which are attributed to the better heat exchange of a long shaft are often in reality due mainly to the unevenness of the short kiln with which they are compared.

(*p*) *Power Consumption.*—When other conditions are kept constant the resistance to the passage of the air and gases through kilns of the same capacity but of different heights varies as the cube of the height. This follows from the fact that the pressure difference required to maintain a given flow of gases varies as the length through which those gases must travel and as the square of their velocity, and the velocity is proportional to the height. For very low velocities the pressure may be proportional to some power of the velocity less than the square, but in kilns with mechanical draught the square law holds. In two kilns of equal capacity and with equal gas flow, one being half the height of the other, the resistance will be eight times as great in the taller one. The power taken by the fan used to force or induce the draught will depend also on the outside connections, etc., and on its efficiency. The former will be much the same in the two kilns, but the efficiency will normally be less in the tall kiln because of the higher pressure or suction. The power-usage factor therefore greatly favours the short kiln.

(*q*) *Crushing of Lime.*—Limestones which burn to soft friable lime are generally considered to be unsuited to tall kilns because the weight of the column of stone above is thought to crush the lime, but there is a misconception in this view because the weight of the stone in a tall narrow kiln is carried mainly on the walls by friction. In a tall kiln the lime is broken by contact with the walls and by the greater distance the burden has to fall at each draw, but even these seldom make a great difference, and the percentage of smalls drawn from a tall kiln is not very much higher than from a short kiln. The determining factor in favour of the short kiln is generally the effect of the small lime on the draught which, in a tall kiln, may be so much reduced as to make the kiln impracticable. Abroad there are tall mixed-feed kilns burning crumbly stone successfully, but they are operated under forced draught at high pressure.

(*r*) *Cost of Lining.*—The weight of refractory lining in a kiln of given capacity increases with the height at a rate somewhat faster than the square root of the height. For example, kilns 50 ft. high by 6 ft. diameter and 25 ft. high by 8 ft. 6 in. diameter have the same capacity, but if each has a 2-ft. thick refractory lining the weight of the lining of the tall kiln is 1.52 times that of the short kiln. The cost of lining is therefore considerably less in the shorter kiln. Maintenance costs will normally show an even wider margin in favour of the short kiln because the lower gas speed favours long life.

(*s*) *Total Cost of Kiln.*—The casing of a steel-cased kiln will cost less in a shorter kiln. For example, two kilns 50 ft. and 25 ft. high may have shells of 10 ft. 6 in. and 13 ft. diameter respectively, which, if of the same thickness,

will be in the ratio of 1.61 : 1 by weight. The short wide kiln would have more costly equipment at top and bottom, whilst its auxiliary equipment would cost less. As a whole the shorter kiln will normally cost distinctly less but the greater proportion of the saving will be in the lining.

(*t*) *Heat Losses Through Wall.*—The loss of heat through the walls of a kiln will be discussed later. It is sufficient here to indicate that for equal capacity and wall thickness the heat loss is proportional to the wall area and therefore to the square root of the height.

(*u*) *Elevating Materials.*—The cost of raising stone to a kiln (and of fuel to a mixed-feed kiln) necessarily increases with the height of the kiln, but the difference is very slight if elevating equipment is used. Of course, a kiln so short that stone may be trammed on top would be cheaper to fill than one where a hoist must be used, but it is seldom that all means of raising the stone are unnecessary.

(*v*) *Peripheral Voids.*—In any kiln the voids amongst the stone in contact with the walls are greater than elsewhere, unless special means are taken to segregate small stone there. The space affected is proportional to the inner circumference of the kiln, and therefore the fraction of the whole cross-sectional area affected is inversely proportional to the diameter or proportional to the square root of the kiln height.

Of the factors favouring a low kiln the most important are those concerned with power consumption and the cost of the lining, which are of considerable weight. To ascertain the most economic height of any proposed kiln is a complicated problem, and in practice it has never been undertaken in the past. Kilns have been built of a height suggested by previous experience or local custom, and if they are right it is mainly by accident. In modern plants the tendency is to increase height, but the necessity for extra height arises mainly from limitations imposed by charging and discharging gear and, in gas-fired kilns, by the distribution of the gas.

### The Kiln Lining.

The lining is subjected to very different conditions at different positions in the kiln. The following discussion applies to vertical kilns burning large stone, but broadly speaking the same points apply to shorter kilns and to rotary kilns. In the uppermost section of a vertical kiln the lining is subject to abrasion from uncalcined stone and, in some kilns, to the impact of pieces of stone which bounce against it during charging ; but such impact should be avoided by proper design. In the burning zone the lining is subjected to heat and to the rubbing of lime, which forms compounds with all the materials ordinarily used for the lining, these compounds being fusible at lower temperatures than the softening point of the lining itself. In the cooling zone the temperature is not excessive, the abrasiveness of burnt lime is low unless it is badly overburnt, and a suitable lining material is easy to find.

THE PREHEATING ZONE.—Limestone varies widely in its abrasiveness. Chalk is generally softer than the softest firebrick, but the majority of limestones are

harder than the softer grades of firebrick and will wear them rapidly, and the hardness of the stone is retained, as it is heated, up to the point at which it is actually calcined to lime. The lime formed is always softer than any ordinary firebrick. It is therefore desirable that the lining of the preheating zone should be highly resistant to abrasion in all kilns except those burning soft chalk.

It is necessary to distinguish between kilns which are charged and drawn throughout the day and night (or which are drawn day and night and have an enclosed storage section for stone above the exhaust gas outlet) and mixed-feed kilns that are charged and drawn by day only so that during the night the burning zone rises, sometimes nearly to the top. In the latter case the upper section of the lining is raised to lime-burning temperature, say 1,000 deg. C., and then suddenly reduced by the introduction of a mass of cold stone. It has, therefore, to withstand abrasion, high temperature, and sudden temperature change, and it is not possible to define the limits of the preheating zone even approximately. In a kiln that is operated continuously the preheating zone will vary in length only to an extent that is dependent on the inevitable unevenness of operation, and there will be no violent fluctuations of temperature. Hard red or blue clay engineering bricks, such as are used for paving purposes, are excellent for the purpose. They resist abrasion and will withstand a temperature up to that of the beginning of calcination. They therefore have a long life in the preheating zone, but ordinarily a sudden change of temperature causes them to spall and they are therefore unsuited to conditions at the top of a mixed-feed kiln drawn and charged by day only. There are, however, fireclays which will produce a brick that is comparable with blue paving bricks in resistance to abrasion whilst being more resistant to sudden changes of temperature. Bricks or blocks of this quality are excellent for use in mixed-feed kilns and, because they are highly refractory, their use need not be restricted to the true preheating zone. They are used to line many kilns throughout. A hard limestone has in the past often been used to line the upper portions of kilns and it is a serviceable material for the purpose, but the cost of dressing it to-day makes it a more expensive lining than an equally serviceable one of clay bricks or blocks. The same remark applies to blocks of other kinds of stone, several of which would be excellent if they were less costly.

THE LIME-COOLING ZONE.—The lime-cooling zone may be lined with firebrick of ordinary quality with a second course of porous low-quality brick or a strong insulating brick. The brickwork as a whole must be strong enough to carry the load of the brickwork above with that part of the load of the kiln contents that is transmitted to it. The top section of the cooling zone, where the lime is normally above 1,000 deg. C., should be lined with the same material as the burning zone, so as to allow for abnormal downward extension of the zone of high temperature.

THE BURNING ZONE.—The production of a refractory material that has an economic life in a modern kiln burning hard pure limestone is of considerable difficulty. The danger of fluxing the best lining at present available·limits the

efficiency attainable in gas-fired kilns, and therefore the problem is not really solved. The ideal kiln would be capable of being operated at the maximum temperature the lime will tolerate for the short period it is at that maximum, and at present there is no known refractory, obtainable at an economic price, which has been proved to withstand those temperature conditions whilst being at the same time mechanically robust.

Refractory materials may be acidic (such as silica) or basic (such as magnesia). Lime, being basic and itself highly refractory, has less tendency to combine with a basic than with a an acidic refractory, and the ideal lime kiln refractory would presumably be basic. · The only basic refractories, other than some very costly ones, are those made of magnesite and dolomite, and all other refractories that are economically possible are composed of silica or alumina, or both.

BASIC REFRACTORIES.—Magnesia refractories are generally pressed and fired bricks made of magnesite which has been dead-burnt at a temperature between 1,450 deg. C. and 1,700 deg. C., mixed with a binding material, such as iron oxide, which combines and causes incipient sintering to bind together the crushed magnesia. The magnesite may itself contain sufficient impurity to cause it to bind together on firing. After they are formed, the bricks should be burnt at a temperature well above that at which they will be used. Magnesia does not combine with lime, and magnesia refractories will withstand without fluxing a temperature higher than the highest kiln temperature. They would therefore be excellent for lime kilns but for their mechanical weakness at high temperature, which results in their rapid abrasion by the lime so that their life is short.

In dead-burning the magnesia is changed to the crystalline form periclase, and crystallisation is promoted by the impurities present, especially iron oxide. Magnesite generally contains lime and silica as impurities, and in burning it is believed that these impurities form relatively low-melting compounds which segregate between the periclase grains and cause weakness at high temperatures. Iron oxide, on the other hand, forms magnesio-ferrite which is relatively refractory, and iron, in moderation, is a less harmful impurity and a useful binding agent. Magnesia refractories are being improved and possibly in the future they will be produced with properties suited to lining lime kilns. Trials have been made in rotary cement kilns which are reported to be encouraging, but at the moment they cannot be considered a practicable lime-kiln lining.

Dolomite for refractory purposes should be a dense rock of composition approximating to that of $CaCO_3.MgCO_3$, but there are many rocks of the right composition which will not form a durable refractory by present methods of production. A good dolomite for refractories may be dead-burnt (i.e., rendered very slow-slaking) at about 1,250 deg. C., but for proper shrinkage a temperature of between 1,500 and 1,700 deg. C. is required, when it shrinks to a dense material and frits together. The frit is crushed, mixed with tar, and rammed into place as a furnace lining, or it may be formed into bricks in the same way as magnesite and the bricks soaked in tar. The tar protects the shrunk dolomite from hydration by atmospheric moisture until the furnace is fired, when it is burnt out. A

rammed dolomite lining is used in the kilns or cupolas in which it is shrunk, and which are operated at a temperature well above any lime-kiln temperature. It would therefore seem to be suited to lime burning, but it is apparently not economic on account of its low resistance to abrasion. Moreover, there is the difficulty of not being able to shut down the kiln without partial or complete destruction of the lining by hydration. Dolomite, chemically, is even better suited than magnesite as a lime kiln refractory, and here again active progress is being made in improving the products.

SILICA-ALUMINA REFRACTORIES.—Refractories composed of silica and alumina may be had ranging in composition from nearly pure silica to nearly pure alumina. The silica refractories are represented by silica bricks and natural siliceous rocks, especially quartzitic schist, having a silica content ranging about 95 per cent. Bricks and blocks made from natural fireclays range in composition from about 50 to 70 per cent. of silica and 15 to 40 per cent. of alumina, and by adding
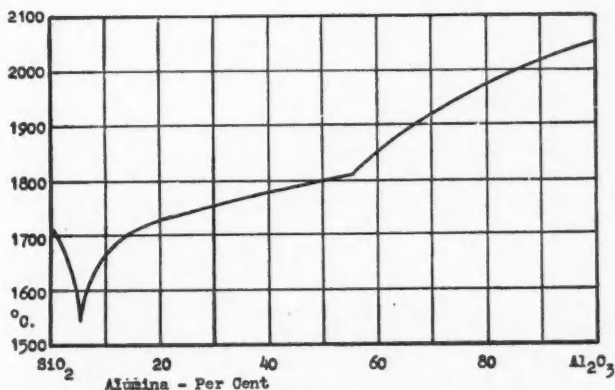


Fig. 17.—Melting Point Curve. The Silica-Alumina System.

bauxite or diaspore to fireclays any composition higher in alumina may be produced. The melting points of silica-alumina mixtures are at a maximum at each end of the composition-melting-point curve, as shown in *Fig.* 17. In commercial refractory materials these melting points are lower owing to the presence of impurities, especially iron oxide, but it is evident that fireclays reasonably low in iron oxide will be sufficiently refractory for the purpose, whilst high-alumina refractories have a wide margin of safety. Mere refractoriness, however, or even strength under load at high temperature, is not of primary importance in the linings of vertical lime kilns. There are ordinarily no wide arches or large openings in the zone of high temperature, and the lining is for the most part under evenly-distributed compression. Failure is due to the combination of the refractory material with lime and the fusion or softening of the resulting compound, which, when soft, is rubbed off by the passing lime.

Alumina is less acidic than silica and it is often contended that this fact makes it a better lime-kiln refractory material than silica. Nevertheless, alumina forms fusible compounds with lime and the minimum point on the melting-point-composition curve of alumina-lime (1,395 deg. C.) is lower than that of silica-lime (1,436 deg. C.), whilst the ternary mixture of alumina, silica, and lime has a still lower range of fusibility. The slagging of a refractory material is not a simple phenomenon which can be predicted from melting points and such simple chemical characteristics as basicity. It depends on the rate of reaction and of diffusion of the melt, and these sometimes run counter to chemical expectations. For example, magnesite bricks are resistant to some highly siliceous slags and, in the same way, some high-silica refractory materials have acquired an excellent reputation for lime-kiln lining.

HIGH-SILICA REFRACTORIES.—A quartzite shale found in Silesia and elsewhere has long been used as a lining for lime kilns. It generally contains 95 per cent. or more silica and about 3 per cent. alumina and has an apparent density of 2.2 or more, indicating a compact structure. It splits into flat blocks with fairly smooth upper and lower faces, but the lateral faces have to be shaped by hand or cut by a diamond saw ; if cut by hand they are not smooth and consequently the vertical joints in the lining are wide ones, whilst if cut by a diamond saw they are costly. This material, in fact, cannot compete in cost with manufactured refractories, and is now used mainly locally whereas formerly it was exported to many countries. It is mechanically resistant to abrasion, and with lime at high temperature it seems to form a viscous glaze which is rubbed off only slowly. It must not be subjected to sudden temperature changes.

Manufactured silica bricks have been used in lime kilns in the United States to a considerable extent, but their success either there or in Europe has not been equal to that of natural quartzite blocks. However, a reliable comparison between them and fireclay or high-alumina refractories as lime-kiln linings does not appear to have been made. Their high expansion and poor resistance to sudden changes of temperature render them unsuitable to use in some kilns.

FIRECLAY REFRACTORIES.—Fireclay refractories are still used in the largest section of nearly all lime kilns and in the burning zone of the majority of kilns. Experience shows that between the limits of composition of natural clays the relation between the percentage of alumina and silica is of relatively minor importance. It is outweighed by properties of the clay and methods of manufacture which influence density and resistance to slagging, and which are found in clays of very varying composition. Some makes of firebricks have acquired a reputation for lime kilns, and the user is better guided by the experience of others than by chemical composition. However, a close texture and sufficient toughness are essential to long life and these are found in all bricks that last well in lime kilns. Good fireclay bricks and blocks are highly resistant to spalling and they will withstand sudden changes of temperature in the upper regions of an intermittently drawn mixed-feed kiln.

HIGH-ALUMINA REFRACTORIES.—Fireclay refractories merge into those

classed as high-alumina through those made from aluminous or bauxitic clays, but generally speaking a refractory containing over 40 per cent. of alumina lies outside the range of ordinary fireclay. Two of the compounds of silica and alumina, sillimanite and mullite, have excellent properties as refractories, and high-alumina refractories aim at a high content of one or other of these minerals. Sillimanite, $Al_2O_3.SiO_2$ (63 per cent. alumina), at high temperatures decomposes to mullite and silica glass, but the rate of decomposition is very slow at lime-burning temperatures. Mullite, $3Al_2O_3.2SiO_2$ (72 per cent. alumina), is stable and shows little softening below its melting point of 1,810 deg. C. One of the earliest successful high-alumina refractories, the German material " Dyamidon," aimed at the mullite composition with an analysis of 72 per cent. alumina.

High-alumina refractories are made from bauxite or diaspore, generally with the addition of some clay. Unlike clays, bauxite on heating continues to shrink up to its melting point, and therefore to avoid shrinkage in use it must be burnt at a temperature well above that to which it will be subjected in use. The poor qualities of some of the earlier high-alumina refractories was due to insufficient attention to this point. They are now obtainable of high quality and are highly refractory and resistant to abrasion and slag action. In a lime kiln they withstand higher temperatures than fireclay or silica blocks, but will flux rapidly with the lime at temperatures much below those they would withstand in the absence of lime and lower than some limes will themselves stand without being overburnt. They are therefore not the final solution of the kiln-lining problem.

OTHER REFRACTORIES.—The more costly refractories, such as chromite, fused alumina (alundum), carborundum, etc., are too expensive to use in lime kilns. Carborundum has been proposed for the retorts in which it has been suggested to burn lime with the simultaneous production of pure carbon dioxide, and also for use in certain parts of kilns of special design, but it is of no general interest. Chromite, too, has been used for the arches of furnace-fired kilns, but the practice has not spread.

REFRACTORY CEMENTS.—The joints between the blocks or bricks are usually the weakest points in the lining of a kiln, and fluxing often begins there. It is generally recognised that the jointing material should be of as nearly as possible the same composition as the brick, but this is not enough. Fireclay bricks and blocks are laid with fireclay joints, and the results are excellent when the joints are very thin, but when the accuracy of shape of the brick or block, or the skill of the bricklayer, is insufficient to ensure thin joints the natural shrinkage of the clay leaves a porous or even cracked joint into which lime penetrates to cause slagging and destruction. The shrinkage is reduced if the jointing material is compounded of ground grog mixed with only sufficient raw clay to make the mixture plastic. In the same way a jointing material for high-alumina bricks consists largely of shrunk bauxite.

There are now many refractory cements on the market which, unlike ordinary fireclay, have the property of hardening on drying or after heating to a relatively low temperature. Many of them consist of grog or ground firebrick or high-

alumina brick wetted with a solution of sodium or potassium silicate or some other low-temperature fluxing agent. On drying they set hard due to the glue-like properties of the silicate, and as the temperature increases the silicate or other agent fluxes with the surrounding firebrick forming a strong bond. Their weakness lies in the reduction in refractoriness due to the presence of the alkali metal. Another type consists of a cement with hydraulic properties mixed with the ground refractory. If properly compounded this type is more refractory than the alkali silicate type, and sets hard without being dried, but it passes through a stage of relatively low strength after it loses its combined water and before sintering begins ; it must therefore be employed with due care. Aluminous cement, mixed with crushed refractory or shrunk bauxite is a cement of this type, and when properly used it has excellent properties. It retains more strength than other hydraulic cements after dehydration, and with most refractories it seems to combine to form compounds with high resistance to spalling and relatively high refractoriness. After further experience in its use it will probably be of much service in lime kilns.

THE SIZE OF REFRACTORY LINING UNITS.—Firebricks are made in standard sizes which, when built into the wall of a kiln, expose an area of one-tenth of a square foot or less, so that at least ten bricks are used for each square foot of wall area. When natural stone is used as a refractory it is cut into much larger sizes, and manufactured refractories are also produced in correspondingly large sizes. The advantages of large refractory units are considerable. The joints in firebrick work are always a source of weakness and the reduction in their number by the use of blocks improves the quality of the work as a whole, provided the quality of the materials is equal. Blocks are often made in sizes such as 12 in. or 15 in. by 12 in. by 6 in. so that only two are required for each square foot of area.

There is difficulty in making large blocks with as a good a shape as bricks, and also a difficulty in drying and firing them so that they are well burnt all through. These difficulties can be surmounted but the blocks necessarily cost more, and it is not unusual to find the first cost of well-made blocks about twice that of an equal weight of bricks. Badly shaped blocks, by necessitating wide joints, eliminate the advantage of their greater area.

## The Thermal Insulation of Kilns.

HEAT LOST THROUGH THE KILN SHELL.—The heat lost through the shell of a lime kiln varies from about 5 per cent. of the total heat supplied in a wide kiln with good insulation, to about 25 per cent. in a narrow and badly insulated kiln. If the amount is estimated as a percentage of the heat actually used in burning lime the losses may be from 10 per cent. in the best kilns up to 50 or 60 per cent. in rotary kilns and inefficient narrow vertical kilns. The capacity of a kiln of given height varies as the square of the diameter, whilst the area through which heat is lost is proportional to the diameter, so that the heat loss per ton of lime varies inversely as the kiln diameter. A kiln of large diameter

is therefore more efficient than a smaller one, other things being equal, or for equal efficiency the small kiln must be much better insulated.

It has been shown* that in all lime kilns more heat enters the preheating zone than can be used there, and that it is the heat available for calcination in the burning zone which controls efficiency. Heat insulation of the preheating zone is therefore redundant unless the heat in the exhaust gases is to be used outside the kiln, and even then, because of the lower temperature of the lining, it is of much less importance than insulation of the burning zone. In the lime-cooling zone heat insulation is necessary for the highest efficiency, but here again the low mean temperature simplifies the problem.

THERMAL INSULATION AND LIFE OF LINING.—The burning zone is therefore the main consideration in lime-kiln insulation and here, using refractories at present available, and with the desire for low production costs, there is a conflict of interests. The effect of perfect insulation behind the kiln lining would be to keep the lining at the same temperature throughout as the temperature of the gases or burning fuel adjacent to the kiln walls ; and the better the insulation, the nearer is the approach to that limit. In a well-insulated kiln the temperature in the burning zone must therefore be limited to one that the lining will withstand with reasonable life. On the other hand, consider a steel-encased kiln without insulation behind the refractory lining. The outside temperature of the lining will depend on the heat transmitted through it, on the coefficient of heat transfer from lining to shell, and the loss of heat from the shell, but in all instances it will be relatively low because of the high rate of transmission in the absence of insulation. Because heat is lost rapidly through the lining the temperature of the inner surface of the latter will always be less than that of the gases or fuel adjacent to it, and consequently the kiln may safely be operated at a higher temperature than the insulated kiln with consequent saving in cost. Furthermore, if the safe temperature is exceeded, the lining, by fluxing away, becomes thinner and therefore transmits more heat, so that its inner surface is cooled more rapidly and will therefore tolerate a still higher kiln temperature. Thus the uninsulated lining, as it wears or fluxes away, becomes more and more resistant, but at the same time the heat loss increases to a corresponding degree. An uninsulated lining will last until it is too thin to support the weight on it, and its actual life may be several times that of a well-insulated lining.

It is therefore evident that there are two sides to the insulation question. Some kiln users prefer to omit all insulation of the burning zone, contending that the loss of heat is more than balanced by the saving in renewal of the lining and the loss of output this entails. In a kiln that tends to burn more fiercely up the walls than elsewhere the relatively high heat loss through an uninsulated lining serves as a partial corrective, but in a kiln designed to avoid overheating the walls it may be necessary to insulate to avoid underburning of the adjacent stone. With improvement in the refractories, too, the reason for omitting insulation loses weight and the modern tendency is towards better insulation.

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* *Cement and Lime Manufacture*, January, 1937.

INSULATING BRICKS.—Insulation may be of two kinds : (1) A course of bricks or blocks behind the refractory lining forming a rigid wall which can carry weight, or (2) A granular, powdered, or fibrous material filling the space between the lining and the shell, or, of course, both may be used.

There are two classes of insulating bricks in general use, and others of minor importance which need not be considered. The first class embodies bricks made of clay—generally fireclay—rendered light in weight and of relatively low thermal conductivity by mixing sawdust or other fine organic matter with the clay before burning. The organic matter burns out leaving the brick with a porous structure which reduces its conductivity. Bricks of the second class are made of infusorial earth (kieselguhr).

Porous clay bricks have not nearly so high an insulating value as the best kieselguhr bricks, but they can be made to withstand high temperatures. The best of them may have a conductivity of about 0.001 C.G.S. units or about 3 B.Th.U. per square foot per hour per degree Fahrenheit temperature difference per inch thickness at about 1,000 deg. C., and they may be used up to about 1,300 deg. C.

Kieselguhr bricks are made by mixing some clay or other bonding material with the earth and burning. The infusorial earth may be merely dried, or it may be calcined at low or high temperature before forming the bricks, and the higher the calcination temperature used the higher the temperature the bricks will withstand without shrinkage. They may be rendered more porous in the same way as clay bricks by the incorporation of organic matter. Moler is an impure infusorial earth containing sufficient clay-like impurity to bond the silica together. The conductivity of kieselguhr bricks varies considerably, but a good brick that can be used up to 1,000 deg. C. may have a conductivity of about 0.0005 at that temperature (1.5 B.Th.U.) and less at lower temperatures, whilst one suitable for lower temperatures may have as low a conductivity as 0.0003 at 500 deg. C. (0.9 B.Th.U.). The crushing strength often approximates to 500 lb. per square inch. If heated to too high a temperature keiselguhr bricks shrink, crack, and lose their insulating value. They also flux readily with lime if they come into contact with it at high temperature.

INSULATING FILLINGS.—The materials used as insulating filling between the lining and the shell of a kiln are varied. Sand, shingle, clinker, broken brick, rubble, etc., are used where there is ample space available and a cheap material of low insulating value is sufficient. As a loose, but efficient, filling kieselghur is employed, and to a less extent pumice and artificial materials of a similar nature. Fibrous insulating materials include asbestos, spun glass, and slag wool, but only slag wool is ordinarily cheap enough for use in a lime kiln. It is a useful packing between firebrick and steel or between insulating brick and steel.

In employing a loose or fibrous filling between the steel shell and the refractory lining it must be remembered that the shell of a kiln is a retaining casing to prevent the outward collapse of the lining. Unless the filling when put in has sufficient rigidity or strength to resist the outward pressure, the lining is liable to crack and spread outward until it meets sufficient retaining pressure.

*(To be continued.)*

# The Thermochemical Basis of Cement Manufacture.

(CONCLUDED)[*]

### By H. ELSNER v. GRONOW.

IN a description of the exothermic effect in the formation of clinker for the purposes of a heat balance it is necessary to distinguish between two types. One is the exothermic effect in the formation of the clinker only at temperatures above 1,200 deg. C. The other includes in addition the exothermic effect due
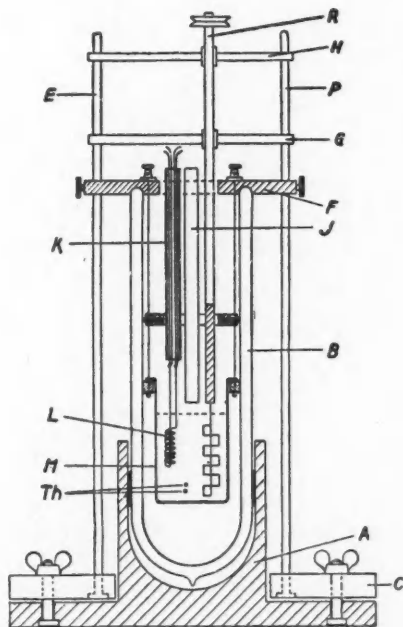


Fig. 3.—Calorimeter for Determining Heats of Solution.

to the metakaolin and the heat of melting in the formation of the flux which do not directly concern clinker formation.

The apparatus used by the author is shown diagrammatically in *Fig.* 3. It gives results which are accurately reproducible due to the good insulation ; H. Wagner[20] has carried out very accurate determinations with this instrument.

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[*] Concluded from April number.

The small calorimeter (120 c.c. capacity) is described in this paper. The larger calorimeter, which is used in the Kaiser-Wilhelm-Institut für Silikatforschung, has a capacity of 180 c.c. of acid solution. The larger calorimeter has a water-jacket outside the Dewar flask (B) which can be kept at a constant temperature by a thermostat and water circulator.

### Wagner's Calorimeter.

The Dewar flask (B) rests in a wooden base (A) the inside of which is protected from corrosion by a coating of shellac or wax. The wooden ring (C) carries the uprights (P) and (E) which pass through two holes in the hard rubber cover (F) and are connected together by the cross-pieces (G) and (H) which carry the bearings for the stirrer. From 30 to 100 mg. of the specimen are introduced into the acid solution through the tube (J) and the temperature rise is measured by three thermocouples connected to a mirror galvanometer. A rise of 0.1 deg. C. corresponds to about 100 mm. on the scale. The readings are converted to temperature by the Regnault-Pfaundler formula.[2] The water equivalent of the calorimeter is determined by the heating coil (L) before and after each experiment. The method used in the United States of obtaining the water equivalent by a standard substance of known heat of solution can be used instead. All the parts of the apparatus in the Dewar flask together with the cover and stirrer can be removed by the frame (C). Another method is to use longer uprights (E) and (P) fixed in the base (A), and to raise (F), (G) and (H) which can be fixed at any height by set screws at the end of a determination.

Three heats of solution in 120 c.c. of acid solution were measured per day. The solution of 34 mg. CaO with a heat of solution of about 1,000 cal. per g. produces a temperature rise of about 0.2 deg. C. Three determinations per day with four determinations of water equivalent did not produce a total temperature rise of more than 1.5 deg. C., so that the procedure was not disturbed by the heat developed. During the same period the room temperature rose slightly. The heats of solution were determined in a mixture of equal parts of dilute hydrofluoric and hydrochloric acids (2.0 to 6.7 normal). On account of the large heat of formation the final products of the reaction are fluorides only (not chlorides), especially $CaF_2$. The concentration of these salts in the solution is so low that in spite of their low solubility they remain in solution and do not separate out. This has the advantage that it is not necessary to know the heat of solution of calcium fluoride, which is very difficult to determine and is not known accurately.

Three different methods were used for determining the exothermic effect in clinker formation from slag and limestone : (1) Subtraction of the heat of solution of the clinker from that of the decarbonated raw meal ; (2) Subtraction of the heat of solution of the clinker from the sum of the heats of solution of the corresponding amounts of blastfurnace slag and calcium oxide in the same acid solutions ; and (3) Determination of the heat of the exothermic reaction at 1,300 deg. C. by means of Hess's Law referred to 1 g. of raw meal = 0.74 g. of clinker :

　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　cal.

(a) The heating of 1 g. of raw meal from 20 deg. C. to 900 deg. C.
　　requires ..　　..　　..　　..　　..　　..　　..　　..　　$- a$

(b) Cooling of the $CO_2$ from 900 deg. C. to 20 deg. C. recovers ..　$+ b$

(c) Heating the decarbonated raw meal from 900 deg. C. to
　　1,300 deg. C. requires ..　　..　　..　　..　　..　　..　　$- c$

(d) The exothermic effect at 1,300 deg. C. recovers　　..　　..　　$+ d$

(e) Cooling 0.74 g. clinker from 1,300 deg. C. to 20 deg. C.
　　liberates ..　　..　　..　　..　　..　　..　　..　　..　　$+ e$

(f) The heat of solution of 0.74 g. clinker at 20 deg. C. is　　..　$+ f$

(g) The heat of solution of 1 g. raw meal at 20 deg. C. is　　..　$- g$

(h) The $CO_2$ liberated (in this case 0.26 g.) from 1 g. raw meal
　　does work against the atmosphere equal to $p$ . $\triangle v$ (1 liter-
　　atmosphere $= 24.2$ cal., therefore for 0.26 g. $CO_2$ the
　　amount is $- 3$ cal.)　　..　　..　　..　　..　　..　　..　　$- h$

Hence we have the exothermic effect

$$d = a - b + c - e - f + g + h$$

By means of the heat requirements already described and the values of $f$ and $g$ given by experiment the exothermic effect $d$ can be found at high temperatures. In experiments carried out recently by the author at the Kaiser-Wilhelm-Institut für Silikatforschung good agreement was obtained among the three methods and the value arrived at for the exothermic effect was 50 to 70 cal. per gram of clinker. It is seen, therefore, that the exothermic effect in the formation of Portland cement from slag and limestone is only about one-half of that for its formation from clay and limestone. This is understandable since certain silicates are already present in the slag during the formation of which heat is liberated.

Since the liberation of heat in the formation of the clinker minerals takes several minutes, and at temperatures of 1,400 to 1,500 deg. C. there are losses due to radiation, a glowing of the mass of material in the sinter zone is not observed in practice as would be expected from calculations of the exothermic effect. The heat required for forming the flux is over 20 cal. per gram of clinker and causes a reduction of the temperature rise due to the exothermic reaction.

### Calculation of the Exothermic Effect from the Composition of the Clinker

This calculation, based on the tests of the author, has not been given because the solution of the problem has been only of scientific interest. The heats of formation of the most important clinker minerals are now known and, using their values, the exothermic effect can be calculated from the analysis without carrying out any experiments on heats of solution. The amounts of the clinker minerals are calculated according to Bogue's method. The formulæ of Lea and Parker, which are useful for other purposes, need not be used here because the differences among the heats of formation of the four most important clinker minerals are small at 1,300 deg. C., and there is hardly any greater precision in the value of the exothermic effect.

The heats of formation of the clinker minerals at 1,300 deg. C. given in *Table* III have been obtained from the difference of the heats of solution at 20 deg. C. and the specific heats from *Table* I.

TABLE III

HEATS OF FORMATION OF CLINKER MINERALS AT 20 DEG. C. AND
1,300 DEG. C. IN CAL. PER GRAM.

|  | | | 20 deg. C. | 1,300 deg. C. | Heat of hydration at 20 deg. C. |
|---|---|---|---|---|---|
| $C_3S$ | .. | .. | 129 | 111 | 126 |
| $C_2S$ | .. | .. | 174 | 147 | 60 |
| $C_3A$ | .. | .. | 77 | 83 | 207 |
| $C_4AF$ | .. | .. | 85 | n.d. | 100 |

In general, the greater the heats of hydration of these compounds the smaller are the heats of formation at 20 deg. C. and at higher temperatures.   The small
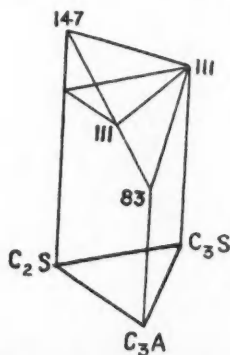


Fig. 4.—Diagram showing the magnitude of the Exothermic Effect
in Clinker Formation for mixtures of the three minerals
$C_2S$, $C_3S$ and $C_3A$.

heat of formation of tetracalciumaluminoferrite is an exception.   A comparison of the heats of formation with the heats of hydration at 20 deg. C. shows that the percentage difference between the heats of formation is greater than that between the heats of hydration.   For large $Fe_2O_3$ content of the clinker (erzzement) the presence of dicalcium ferrite must be taken into account ; the heat of formation of dicalcium ferrite is about 80 cal. per gram at 20 deg. C., while that of $CaO.Fe_2O_3$ is 87 cal. per gram.

In *Fig.* 4 the exothermic effects are drawn as perpendiculars from the corners of the triangle $C_3S$, $C_2S$, $C_3A$.   If a plane is taken which includes the three points 83, 111 and 147, then any point in the plane corresponding to the composition of the clinker gives the exothermic effect as the perpendicular distance of the point above the plane $C_3S$, $C_2S$, $C_3A$.   A series of clinkers is obtained having the same exothermic effect as tricalcium silicate (shown in *Fig.* 4 by the

line III—III) ; e.g. a clinker with 21.4 per cent. $SiO_2$, 9.8 per cent. $Al_2O_3$ and 68.8 per cent. CaO, or 52 per cent. $C_3S$, 22 per cent. $C_2S$ and 26 per cent. $C_3A$. For practical use the following method of calculation of the exothermic effect in clinker formation from clay and limestone over 900 deg. C. may be employed. (1) The amounts of the clinker minerals are calculated by Bogue's method. (2) The amounts of clinker minerals in grams contained in 1 kg. of clinker are multiplied by the heats of formation in *Table* III and the results added together. (3) The metakaolin content of the raw meal is obtained by multiplying the percentage of $Al_2O_3$ in the clinker by 2.17. If, in the decomposition of 1 gram of dehydrated clay substance into the free crystallised oxides, 96 cal. per gram are liberated* and practically all the alumina in the clinker comes from kaolin and no other compound, then the exothermic effect due to metakaolin calculated for 1 gram of clinker with $x$ per cent. $Al_2O_3$ is

$$2.17 \times 96 \times \frac{x}{100} \text{ cal.} = 2x \text{ cal.}$$

Hence the exothermic effect in the clinker is increased by 19.6 cal. per gram due to the metakaolin if the clinker contains 9.8 per cent. $Al_2O_3$. For a clinker with 5 per cent. $Al_2O_3$ the exothermic effect is increased by 10 per cent., i.e. the true exothermic effect at 1,300 deg. C. will be about 10 per cent. greater if the exothermic effect of metakaolin is taken into account.

The exothermic effect in the formation of aluminous cement (in cal. per gram) is about the same as that for Portland cement. According to O. F. Honus, the heat of formation of monocalcium aluminate (CA) from CaO and $\gamma$-$Al_2O_3$ is 105.2 cal. per gram (16.62 kg. cal. per Mol) ; the value usually taken has been 81 cal. per gram as given by Tschermobajeff. For the same reaction, but using $\alpha$-$Al_2O_3$ instead of $\gamma$-$Al_2O_3$, the heat of formation is only 22.3 cal. per gram (3.52 kg. cal. per Mol). If only the crystallisation of amorphous alumina to the $\gamma$-modification is taken into account in the exothermic effect of the alteration of metakaolin between 920 and 1,020 deg. C. (16 kg. cal. per Mol metakaolin) the heat of formation of CA will be about 16 kg. cal. per Mol greater if it is amorphous alumina and not $\gamma$-alumina which inverts. In this case the maximum heat of formation of 32.6 kg. cal. per Mol = 206 cal. per gram is obtained for CA.

If the alumina in the raw material for the manufacture of aluminous cement is present as $Al_2O_3.3H_2O$ (Bauxite), 8 kg. cal. per Mol are required for dehydrating it, or 78 cal. per gram of alumina. In calculating the heat balance for the manufacture of aluminous cement this must be taken into account.

### Heat Required for Forming the Flux at over 1,200 deg. C.

So far this has not been taken into account in calculations of heat balances. E. Schott stated in a paper in the proceedings of the Verein Deutscher Portland-zementfabrikanten (1932, pp. 38–39) that, according to his observations and those

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* The heat of crystallisation of amorphous silica is included.

of Gilbert, there was no exothermic effect to be allowed for in the heat diagrams. The cause of this paradox is that the endothermic effect in the dehydration of kaolinite at about 500 deg. C. is greater than had been assumed and that heat is required for forming the flux in the clinker (about 24 per cent. of the total mass at 1,400 deg. C.) which these authors did not take into account. A large part of the flux present in the clinker at 1,400 deg. C. can in practice be super-cooled to a glass, and the heat in forming it above 1,200 deg. C. is not recovered as heat of crystallisation but remains in the form of a high specific heat of the glass.[4]

There is only one way of obtaining the higher energy content of clinker which contains an amorphous ground mass (glass)† as a difference between this and the crystalline material. The composition of the flux is calculated at a high temperature, e.g. 1,400 deg. C. according to Lea and Parker.[12] This flux is made and its heat of solution measured after quenching. From this is subtracted the heat of solution of the devitrified flux, and the heat of crystallisation at 20 deg. C.
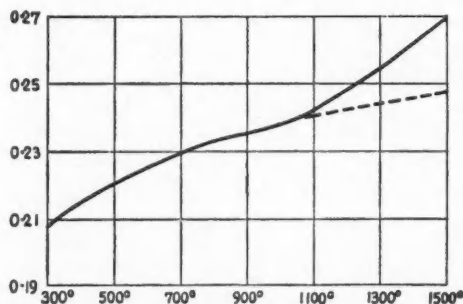


**Fig. 5.—Mean Specific Heat of Portland Cement Clinker according to H. E. Schwiete. The dotted line refers to $C_3S$.**

is obtained. The value of this is only 20 cal. per gram for a flux of the following composition : 35 per cent. $C_4AF$ ; 32 per cent. $C_3A$ ; 5 per cent. $C_5A_3$ ; 18 per cent. $C_2S$ ; 8 per cent. MgO ; 2 per cent. alkalis.

H. E. Schwiete[7] has attributed the increase of the mean specific heat of Portland cement clinker above 1,100 deg. C. to the appearance of an increasing amount of a liquid phase in the clinker with rising temperature (*Fig.* 5). According to these measurements the mean specific heat $\bar{c}$ (at 1,400 deg. C.) of the crystallised clinker, which may be considered equal to that of pure tricalcium silicate (see

† The attempt to obtain the energy difference at 20 deg. C. by measuring the heats of solution of the rapidly quenched clinker and the material ignited at 1,100 deg. C. for a long time to devitrify it fails because the result is obtained as a difference between two large amounts of heat and lies within the experimental error of the method of determination.

*Table* I), is 0.246, and that of rapidly cooled clinker with a flux content of at most 24 per cent. is 0.262, so that the energy content of the rapidly cooled product is $0.16 \times 1,380 = 22 \pm 2$ cal. per gram greater than that of the crystallised material. This heat item should not really be described as heat of crystallisation as it does not agree in practice with the complete crystallisation of the 24 per cent. of flux in the clinker which would, according to this, have a heat liberation of about 93 cal. per gram of flux.

The rise in the true specific heat of glasses of about 60 to 70 per cent. at the softening point, i.e. when the viscosity drops below $\eta = 10^{13}$ c.g.s. units as is universally observed, accounts for the large liberation of heat during the cooling of clinker with an amorphous ground mass compared with that of the completely crystallised products. If the temperature at which the glass goes over into the softened material of high viscosity is 1,000 deg. C. for the flux under consideration, the increased liberation of heat amounts to $400 \times 0.18 \times 24$ per cent. $= 17$ cal. per gram of clinker if the rise in the true specific heat is 0.18 cal. per gram ($= \frac{2}{3} \times 0.27$). From 20 deg. C. to the softening temperature the true specific heats of the glass and crystalline material have been found to be nearly equal in practice. The difference in energy content between 1 gram of quenched clinker containing 22 to 24 per cent. supercooled flux and the slowly cooled material is 5 cal. at 20 deg. C., but $5 + 17 = 22$ cal. per gram at 1,400 deg. C. This value of 22 cal. corresponds to the larger value of the energy content of clinker at high temperatures compared with crystallised tricalcium silicate as determined by H. E. Schwiete (*Fig.* 5).

It can be assumed from experiments on the thermodynamics of the glassy state, which come within the framework of this discussion, that this value calculated from the difference in energy contents at 20 deg. C. and from the difference of the specific heats above the softening temperature agrees well with the heat of melting of the flux in this clinker at 1,400 deg. C.

### The Complete Heat Balance for Burning 1 kg. of Portland Cement Clinker.

This heat balance is calculated for an ideal process and is based on the heat values given in this paper.

RAW MATERIAL.—The raw meal considered consists of 75.8 per cent. calcium carbonate and 16.3 per cent. clay material. The clay material is taken as consisting of pure kaolinite $Al_2O_3.2SiO_2.2H_2O$ and 7.9 per cent. $SiO_2$ (quartz). For simplicity the magnesium oxide and the compounds containing iron are neglected. The heat values for these are given in *Table* IV.

PRODUCT.—A normal Portland cement clinker with 66 per cent. CaO, 24 per cent. $SiO_2$ and 10 per cent. $Al_2O_3$.

HEAT REQUIREMENT.—This is calculated for 1 kg. of clinker corresponding to 1,553 grams of raw meal. The 253 grams of kaolinite contained in 1,553 grams of raw meal lose 2 molecules of water (35 grams) during burning and 1,177 grams of calcium carbonate give off 518 grams of carbon dioxide during decarbonation.

## TABLE IV.

HEATS OF FORMATION AND INVERSION IN THE THERMOCHEMISTRY OF CEMENT COMPOUNDS AT 20 DEG. C. AND AT THE REACTION OR EQUILIBRIUM TEMPERATURES IN CAL. PER GRAM.

| Reaction. | Heat of Formation at 20 deg. C. of 1 gram of Material and its Molecular Weight. | Liberation of Heat at the Equilibrium Temperature (T). | T deg. C. |
|---|---|---|---|
| $CaO + CO_2 = CaCO_3$ | 100 | 425 | $396 \pm 3$ | 907 |
| $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$ | $100 + 18$ | 270 | | |
| $MgO + CO_2 = MgCO_3$ | 84.3 | 215 | $195 \pm 8$ | |
| $CaO + SO_3 = CaSO_4$ | 136 | 690 | | |
| $2CaO + SiO_2\text{-Gel} = \beta\text{-}C_2S$ | 172 | 193 | | |
| $2CaO + SiO_2 \text{ cryst.} = \beta\text{-}C_2S$ | 172 | 174 | 147 | 1,300 |
| $\beta\text{-}C_2S \to \gamma\text{-}C_2S$ | 172 | 6.0 | 8.8 | 675 |
| $2CaO + SiO_2\text{-Gel} = \gamma\text{-}C_2S$ | 172 | 199 | | |
| $SiO_2\text{-Gel} \to \beta\text{-}SiO_2$ | 60 | 56 | | |
| $\alpha\text{-}SiO_2 \to \beta\text{-}SiO_2$ | 60 | ca. 3 | 3.1 | 572 |
| $Al_2O_3 . 2SiO_2 \to Al_2O_3 + 2SiO_2$ | 222 | $72 \pm 10$ | $72 \pm 10$ | ca. 960 |
| $AS_2 + 2H_2O = Al_2O_3 . 2SiO_2 . 2H_2O$ | 258 | 135—145 | 213—223 | ca. 450 |
| $4CaO + \gamma\text{-}Al_2O_3 + Fe_2O_3 = C_4AF$ | 486 | $85 \pm 2$ | ? | 1,415 |
| $3CaO + SiO_2\text{-Gel} = C_3S$ | 228 | 144 | | |
| $3CaO + \beta\text{-}SiO_2 = C_3S$ | 228 | 129 | 111 | 1,300 |
| $\beta\text{-}C_2S + CaO = C_3S$ | 228 | ca. 2 | 0 | ca. 1,300 |
| $3CaO + Al_2O_3 = C_3A$ | 270 | 77 | 83 | 1,300 |
| $C_3A + 6H_2O = C_3A . 6H_2O$ | 378 | $210 \pm 3$ | | |
| $CaO + \gamma\text{-}Al_2O_3 = CA$ | 158 | 105 | ? | 1,300 |
| $CaO + \alpha\text{-}Al_2O_3 = CA$ | 158 | 22 | 19 | 1,300 |
| $CaO + Al_2O_3 \text{ (amorph)} = CA$ | 158 | max. 206 | — | — |
| $CaO + Fe_2O_3 = CF$ | 216 | 87 | ? | 1,210 |
| $2CaO + Fe_2O_3 = C_2F$ | 272 | ca. 80 | ? | 1,436 |
| $\gamma\text{-}Al_2O_3 + 3H_2O = 2Al(OH)_3$ | 150 | 64 | | |
| $\gamma\text{-}Al_2O_3 + 1H_2O = 2(AlO . OH)$ | 60 | 86 | | |
| $\gamma\text{-}Al_2O_3 \to \alpha\text{-}Al_2O_3$ (Roth and Troitzsch) | 102 | 76 | ? | |
| $MgO + H_2O = Mg(OH)_2$ | 40.3 | 203/1 g MgO[1] | 434/1 g MgO[2] | 200 |
| $CaO + H_2O = Ca(OH)_2$ | 74 | 278/1 g CaO | ? | 547 |
| $H_2 + F_2 = H_2F_2$ | 40 | 6,350 | | |
| $H_2 + Cl_2 = 2HCl$ | 36.5 | 1,178 | | |
| $H_2 + O_2/2 = H_2O$ | 18 | 3,793 | | |

[1] Heat of hydration of MgO at 20 deg. C. according to Lea.

[2] According to Büssem and Köbrich (*Zeitschr. f. Physikal Chem.*, Vol. 17, p. 315, 1932), the heat of formation of $Mg(OH)_2$ from MgO and $H_2O$-vapour at 200 deg. C. is 17,500 cal./Mol.

The total loss in weight during burning is therefore $518 + 35 = 553$ grams for 1,553 grams of raw meal.

(I) Heating the raw meal (1,553 grams) from 20 to 450 deg. C. (the dehydration point of the kaolinite) requires :

    (a) for heating 253 g. clay material from 20 to 450 deg. C. :    kg. cal.

        $253 \times 430 \times 0.284$ cal. .. .. .. .. .. $= 31$

    (b) for heating 123 g. $SiO_2$ from 20 to 450 deg. C. : $123 \times 430$

        $\times 0.240$ cal. .. .. .. .. .. $= 13$

    (c) for heating 1,177 g. $CaCO_3$ from 20 to 450 deg. C. :

        $1,177 \times 430 \times 0.248$ cal. .. .. .. .. .. $= 125$

                                  $= 169$

(II) Heat of dehydration of kaolinite (253 g.) : $253 \times 223$ cal.   =   56

(III) For heating the dehydrated raw meal from 450 to 900 deg. C. :

    (a) Heating 217.7 g. metakaolin from 450 to 900 deg. C. : $217.7 \times 450 \times 0.277$ cal. .. .. .. .. ..   =   27

    (b) Heating 123 g. quartz from 450 to 900 deg. C. : $123 \times 450 \times 0.286$ cal. .. .. .. .. ..   =   16

    (c) Heating 1,177 g. $CaCO_3$ from 450 to 900 deg. C. : $1,177 \times 450 \times 0.254$ cal. .. .. .. .. ..   =   150

(IV) The endothermic effect in decarbonating the calcium carbonate in the raw meal at 900 to 910 deg. C. : $1,177 \times 396$ cal.   =   466

(V) Heating the decarbonated raw meal from 900 to 1,400 deg. C.:

    (a) Heating $1,177 \times 0.56$ g. = 660 g. CaO from 900 to 1,400 deg. C. : $660 \times 500 \times 0.226$ cal. .. .. ..   =   75

    (b) Heating 218 g. metakaolin from 900 to 1,400 deg. C. : $218 \times 500 \times 0.291$ cal. .. .. .. .. ..   =   32

    (c) Heating 123 g. $SiO_2$ from 900 to 1,400 deg. C. : $123 \times 500 \times 0.283$ cal. .. .. .. .. ..   =   17

(VI) Formation of 24 per cent. flux at about 1,400 deg. C. ..   =   22

<div align="right">Total .. .. = 1,030 ± 6</div>

HEAT RECOVERY—

(I) Exothermic effect in the crystallisation of the amorphous constituents in the metakaolin at about 960 deg. C. : $0.22 \times 72$ kg. cal. ± 10 cal. .. .. .. .. .. .. .. ..   =   16

(II) Exothermic effect in clinker formation[21] .. .. ..   =   119

(III) Cooling the clinker from 1,400 to 20 deg. C. : $1,380 \times 0.261$   =   360

(IV) Cooling the gaseous carbon dioxide from 900 to 20 deg. C. : $517 \times 880 \times 0.258$ cal... .. .. .. .. .. ..   =   117

(V) Cooling water vapour given off from the kaolinite in the raw meal at 450 deg. C. :

    (a) to 100 deg. C. : $35.31 \times 350 \times 0.478$ cal. .. .. ..   =   6

    (b) Condensation at 100 deg. C. : $35.3 \times 539$ cal. .. ..   =   19

    (c) Cooling 35.3 g. water from 100 deg. C. to 20 deg. C. .. =   3

<div align="right">Total .. .. = 640</div>

The total amount of heat recovered from the processes which liberate heat is 640 ± 6 kg. cal. per kg. of clinker. The difference between the heat requirement and the heat recovery is therefore $1,030 - 640 = 390 ± 12$ kg. cal. per kg. of clinker.

Eitel and Schwiete[22] obtained the value of 437 kg. cal. using earlier values for the heat constants. They used a raw meal of the same composition as the present author and hence the results can be compared. The burning of Portland cement in an ideal kiln having no external heat losses therefore requires about 11 per cent. less heat when calculated from the new data than when calculated from the data available in 1932.

TABLE V.

MEAN SPECIFIC HEATS $\bar{c}$ FOR THE TEMPERATURE RANGES REQUIRED IN
MAKING HEAT BALANCES.

|  | Deg. C. | | | | |
|---|---|---|---|---|---|
|  | 20–450 | 450–900 | 900–1,400 | 20–900 | 20–1,400 |
| $CaCO_3$ .. .. .. | 0.248 | 0.254 | — | 0.266 | — |
| $SiO_2$ .. .. .. | 0.240 | 0.286 | 0.283 | 0.263 | 0.270 |
| CaO.. .. .. .. | — | — | 0.226 | 0.213 | 0.218 |
| $Al_2O_3 . 2SiO_2 . 2H_2O$ .. | 0.280 | — | — | — | — |
| $Al_2O_3 . 2SiO_2$ .. .. | 0.238 | 0.277 | 0.291 | 0.258 | 0.270 |
| Clinker .. .. .. | — | — | 0.305 | 0.236 | 0.261 |
| $CO_2$ .. .. .. | — | — | — | 0.258 | — |
| $H_2O$-steam.. .. .. | 0.478[1] | — | — | — | — |

[1] For 100 to 450 deg. C. at $p = 760$ mm. Hg.

For some years past (e.g. Bussmeyer, 1930) the endothermic effect in the dehydration of the clay, which amounts to 14 per cent. of the total heat requirement in the heat balance given, has not been taken into account. An economy can be effected in connection with this item by a suitable waste-heat recovery process and hence there is no need to consider the earlier heat balances.

Lacey and Woods[23] published a heat balance for a rotary kiln in 1935. They used corrected earlier thermochemical data taken from the International Critical Tables and the work of R. D. Pike.[16] They obtained an external heat loss of 8.3 per cent. of the total fuel used by measurements on a kiln fitted with thermocouples in the lining and on the shell. But from the total heat balance of the kiln a larger figure than 6.0 per cent. for this was not obtained.

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[21] Elsner von Gronow und Schwiete, *Zement*, Vol. 24, No. 35, 1935.
[22] Eitel und Schwiete, *Zement*, Vol. 21, No. 25, 1932.
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## RECENT PATENT.

### Cements.

454,749. Krupp Akt.-Ges., F., Essen, Germany. Jan. 15, 1936.

In the manufacture of metallurgical cement, i.e. blastfurnace, iron Portland, and like cements in which blastfurnace slag is incorporated during manufacture, the raw materials are sintered on a bed of undried slag sand on a blast grate, and the sintered material is then finely ground. The raw materials may be loosened before sintering by quickly stirring or whipping while moisture is added, or the structure may be loosened by adding material having a coarser grain, e.g. sinter returns. The fuel may be mixed with the raw materials.

## PATENT.